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March 29, 1985

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Energy, Mines and Resources
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RE: **EVALUATION OF ADSORBENTS FOR TREATING STABLE OIL/WATER/MINERAL EMULSIONS**

Dear Marc:

Please find enclosed a final draft copy of the final report for this project. The information presented in the Phase II interim report has been retained in this report and the results obtained in the latter part of Phase II have been added and are found in Sections 2.4.1.4, 2.5, 2.6, 3.4.1.4, 3.5 and 3.6. A technological evaluation of all of the major processes examined in Phase II of this study has been completed and is presented in Section 4. Specific recommendations for further study on produced water emulsion destabilization using metallic coagulants have been made and are included in Section 5.

I hope you find this report satisfactory and I look forward to our meeting on Wednesday April 3rd to discuss this report and our recommendations for future studies.

Yours truly,

Heather Donison

H. Donison
Environmental Scientist

HD:jd
Encl.

TABLE OF CONTENTS

		Page No.
1.0	**INTRODUCTION**	1 - 1
2.0	**EXPERIMENTAL PROCEDURES**	2 - 1
	2.1 EMULSION CHARACTERIZATION	2 - 1
	2.2 SLURRY CONTACTOR/CLARIFIER ADSORPTION TESTS	2 - 1
	2.3 PRELIMINARY ADSORBENT REGENERATION TESTS	2 - 2
	2.4 ADVANCED ADSORPTION/REGENERATION TESTS	2 - 4
	2.4.1 MINTO COAL	2 - 4
	2.4.1.1 ADVANCED ADSORPTION TESTS	2 - 4
	2.4.1.2 ADVANCED REGENERATION TESTS	2 - 4
	2.4.1.3 LEACHING STUDIES	2 - 5
	2.4.1.4 DESTABILIZATION/FILTRATION TEST	2 - 6
	2.4.2 FLY ASH	2 - 8
	2.4.2.1 ADVANCED ADSORPTION TESTS	2 - 8
	2.4.2.2 ADVANCED REGENERATION TESTS	2 - 8
	2.5 COAGULATION DESTABILIZATION/PRECIPITATION TESTS	2 - 8
	2.6 ALTERNATE ADSORBENT TESTS	2 - 9
3.0	**RESULTS AND DISCUSSION**	3 - 1
	3.1 EMULSION CHARACTERISTICS	3 - 1
	3.2 CONTACTOR/CLARIFIER ADSORPTION BEHAVIOR	3 - 1
	3.3 PRELIMINARY ADSORBENT REGENERATION TESTS	3 - 5
	3.4 ADVANCED ADSORPTION/REGENERATION TESTS	3 - 11
	3.4.1 MINTO COAL	3 - 11
	3.4.1.1 ADSORPTION OF PRESCREENED MINTO COAL	3 - 11

TABLE OF CONTENTS (CONT'D)

	Page No.
3.4.1.2 REGENERATION OF PRE-SCREENED MINTO COAL	3 - 11
3.4.1.3 MINTO COAL LEACHING STUDY	3 - 14
3.4.1.4 DESTABILIZATION/FILTRATION TEST	3 - 20
3.4.2 FLY ASH	3 - 22
3.4.2.1 ADVANCED ADSORPTION TESTS	3 - 22
3.4.2.2 ADVANCED REGENERATION STUDIES	3 - 22
3.5 COAGULANT DISTABILIZATION/PRECIPITATION TEST	3 - 24
3.5.1 EFFECT OF COAGULANT DOSAGE	3 - 24
3.5.2 EFFECT OF INORGANIC CATION TYPE	3 - 24
3.6 ALTERNATIVE ADSORBENTS	3 - 29
4.0 TECHNICAL EVALUATION	4 - 1
4.1 MINTO COAL	4 - 1
4.2 FLY ASH	4 - 2
4.3 COAGULANTS	4 - 3
5.0 CONCLUSIONS AND RECOMMENDATIONS	5 - 1
5.1 CONCLUSIONS	5 - 1
5.2 RECOMMENDATIONS	5 - 3
REFERENCES	R - 1
APPENDIX A - ANALYTICAL PROTOCOL	A - 1

EXECUTIVE SUMMARY

The objective of this study was to make a preliminary assessment of the technical and economic feasibility of treating emulsions from in-situ bitumen/heavy oil recovery operations for recovery of the oil and preparation of suitable water for boiler feed utilizing some novel adsorbents developed within the Separation and Characterization laboratory of Energy Mines and Resources Canada.

This project was completed in two phases. In the first phase, a report was prepared which focussed on the characterization of the adsorption behaviour of the novel adsorbents, determination of an appropriate mode of operation for these adsorbents and of the approximate cost for producing water for boiler feed. Three novel adsorbents (fly ash, red mud, Minto coal) were evaluated with respect to their potential for the treatment produced water. Fly ash and Minto coal were determined to have the best potential based on isotherms for total suspended oil (TSO) removal at two pH levels. The most appropriate mode of operation for these two adsorbents was determined to be slurry contact followed by precipitation clarification.

During the second phase of this study, work was focussed on the development and characterization of the slurry contact and clarification process for the treatment of produced water utilizing the novel adsorbents Minto coal and fly ash and the development of methods that could be used for the recovery of the adsorbed oil and regeneration of the spent adsorbents. Conclusions were drawn from the results of these studies concerning the mechanism of oil removal by Minto coal. The mechanism of oil removal by Minto coal was determined

to be emulsion destabilization and precipitation caused by a coagulation type reaction with iron released from the coal rather than an adsorption of oil on organics on the coal surface as originally believed.

This study has shown that virgin Minto coal can effectively destabilize wellhead emulsions and that the oil can be separated from the destabilized emulsion by either precipitation or filtration. Residual TSO levels from precipitation treatment were approximately 200 mg/L while from filtration treatment residual TSO levels were 0.2 mg/L. Furthermore the Minto coal can be readily recovered in these processes by a screening step however the potential for reuse of the coal is limited to less than four cycles. The separated oil can be recovered from the precipitation sludge or filtration column by the use of de-emulsifying chemicals and solvents respectively. Technically and economically the most limiting factor in these processes is the complex and expensive coal slurrying and screening procedures.

Fly ash was shown to have limited technological promise for use in the treatment of produced water emulsions. Although fly ash was shown to destabilize wellhead emulsion, excessive energy input is required to promote effective settling of oil and fly ash deposition on the filtration media is a major obstacle to be overcome before filtration could be a viable option.

The most technologically and economically promising results were obtained in multivalent coagulant destabilization/precipitation tests performed to follow up the conclusion drawn regarding the mechanism of oil removal by Minto coal. In these tests trivalent

metallic coagulants (ferric chloride, alum, vanadium chloride) were shown to be very effective for the destabilization of wellhead emulsion. Upon precipitation of the emulsion destabilized by these coagulants the residual TSO level was in the order of 100 mg/L. Further process development would be required before an accurate technological and economic assessment of this process can be completed.

Based primarily on the results of the coagulant tests a number of recommendation for further study have been made. These recommendations concern the development of processes utilizing trivalent coagulants for the destabilization of produce water emulsions. Further studies should focuss on the optimization of the coagulation process and development of precipitation and filtration processes for the effective separation of the destabilized oil and recovery of this oil for further processing.

1.0 INTRODUCTION

This report presents the results of the second phase of a two phase project contracted to ZENON Environmental Inc. by the Department of Supply and Services Canada (DSS) on behalf of Energy Mines and Resources Canada.

The objective of this study was to make a preliminary assessment of the technical and economic feasibility of treating emulsions from in-situ bitumen/heavy oil recovery operations for recovery of the oil and preparation of suitable water for boiler feed utilizing some novel adsorbents developed within the Separation and Characterization laboratory of Energy Mines and Resources Canada.

Produced water from the in-situ recovery of heavy oil/bitumen is contaminated with suspended solids, suspended and emulsified oil, dissolved organics and numerous inorganic ions. Since recovery operations in western Canada are located in water-short or environmentally sensitive areas, it is desirable to recycle produced water for treatment and reuse as boiler feedwater. The conventional produced water treatment scheme involves steps for the removal of suspended and emulsified oil, silica, and hardness removal. Adsorption is a potentially suitable unit process for fine (suspended and emulsified) oil removal. The conventional oil field method for fine oil removal is induced gas flotation (IGF). Extensive operating experience combined with the fact that this method is effective for both solids and oil removal makes IGF the current method of choice for fine emulsified oil removal. However, the energy requirements, float handling procedures and the need for chemicals, chemical handling, and chemical storage result in high operating costs.

This project was completed in two phases. In the first phase, a report was prepared which focussed on the characterization of the adsorption behaviour of the novel adsorbents, determination of an appropriate mode of operation for these adsorbent and of the approximate cost for producing water for boiler feed. Three novel adsorbents (fly ash, red mud, Minto coal) were evaluated with respect to their potential for the treatment produced water. Fly ash and Minto coal were determined to have the best potential based on isotherms for total suspended oil (TSO) removal at two pH levels (equilibrium solution pH, pH = 3.8). Minto coal at low pH had a TSO loading of 2.5 g/g at a TSO equilibrium concentration fo 30 g/L and fly ash with no pH adjustment had a loading of 1.5 g/g at the same TOS equilibrium concentration. Although the red mud had an extremely high equilibrium TSO loading (4.5 g/g at 30 g/L TSO) at low pH, the excessive amounts of acid required to reduce the pH to this level makes this adsorbent pH combination uneconomical.

The reaction kinetics and the physical properties which are significant for adsorption applications were determined for the Minto coal and fly ash. The reaction kinetics were very fast and equilibrium was reached within 5 minutes for TSO and filtered organic carbon (FOC) adsorption.

Based on these initial laboratory evaluation, the mode of operation, recommended for further study, for the treatment of produced water using either Minto coal or fly ash is slurry contact and clarification followed by an adsorber-filter. In phase I a preliminary economic assessment of these processes was made and the conclusion was that the economic viability of these processes required

that a technological and economic method for the recovery of the adsorbed oil and regeneration of the spent adsorbents be developed.

Based on the results of Phase I, the objectives of Phase II were defined as follows:

i) To develop and characterize the slurry contact and clarification process for the treatment of produced water utilizing the novel adsorbents Minto coal and fly ash.

ii) To determine and develop a method or methods that could be used for the recovery of the adsorbed oil and regeneration of the spent adsorbents.

iii) To assess the technical and economic feasibility of treating wellhead emulsions from in-situ bitumen/heavy oil recovery operations using the methods developed in objectives i) and iii).

During the course of the Phase II study, conclusions were drawn concerning the mechanism of oil removal by Minto coal which affected and broadened the scope of this study. The oil removal by Minto coal was determined to be emulsion destabilization and precipitation caused by release of multivalent cations from the coal. During discussions with the Scientific Authority for this project, it was agreed that the technological implications of this conclusion would be investigated. Thus a further objective of this study was defined as follows.

iv) To develop the use of multivalent cations for the treatment of produced water for oil recovery and the production fo boiler feed water.

Under the limited budget left in the project at the time objective iv) was added, the study was designed to be a screening type study to give direction for further research on coagulant treatment of produce water. Furthermore to free resources for this study objective iii) was reduced to a primarily technical assessment.

2.0 EXPERIMENTAL PROCEDURES

2.1 Emulsion Characterization

Liter samples of wellhead emulsion were supplied by Texaco Canada Resource Ltd. These samples had been collected at the Ft. McMurray pilot plant, over a six month time span in the latter half of 1983. The samples were from a number of different wells operating at different temperatures and pressures.

To obtain an "average" sample all of the liter samples were composited. The composite sample was analyzed for the following parameters:

- total suspended oil (TSO)
- calcium
- magnesium
- iron
- alkalinity

The analytical procedures are included in Appendix A. Before analysis, the floating free oil and the settled material were removed from the samples.

2.2 Slurry Contactor/Clarifier Adsorption Tests

In order to obtain spent adsorbents for preliminary regeneration studies. The adsorbents were contacted with the produced water in bench-scale batch contactor/clarifiers. For each adsorbent, 6 dosages (30 - 80 g/L) were used such that an isotherm could be developed for the Phase II composite emulsion under contactor/clarifier conditions. The contactor/clarifiers used in this study were square (9.5 x 9.5 cm), glass, one liter jars. Each jar was

stirred at 100 rpm with a paddle connected to an adjustable speed electric motor. The value of the velocity gradient (G) is $150s^{-1}$ under these conditions.

After the rapid mix contact period, the adsorbents were allowed to settle and the settling characteristics observed. After four hours of settling the supernatant was decanted, the pH and the total suspended oil (TSO) of the supernatant determined, and the TSO isotherm for each adsorbent determined. For each adsorbent, the concentrated oil sludges containing the spent adsorbent from the jars treated with different adsorbent dosages were composited to obtain an average sample for the regeneration studies.

2.3 Preliminary Adsorbent Regeneration Tests

In order to determine the most promising regeneration methods, a large number of relatively simple, regeneration tests were performed. These tests were not designed to be rigorously quantitative but were designed to indicate optimum paths for further investigation. For both of the spent adsorbents studied the following tests were performed.

TEST #1 Direct Heating

Spent adsorbent sludge was dewatered overnight on a paper filter. The filtercake was then heated on a slanted glass surface at incremental temperatures between 50°C and 210°C and any changes observed.

TEST #2 Boiling Water Wash

25 mL of spent adsorbent sludge was mixed vigorously for two

minutes with 25 mL of HPLC grade water at 100°C. The mixture was then observed over a two hour settling period.

TEST #3 Caustic Water Wash

25 mL of spent adsorbent sludge was mixed vigorously for two minutes with 25 mL of 2N NaOH solution at 100°C. The mixture was then observed over a two hour settling period.

TEST #4 Screening

50 mL of spent adsorbent sludge was poured on a 200 mesh screen and the screen gently shaken. The amount and nature of the sludge retained on the screen and passed through the screen was observed.

TEST #5 Centrifugation

15 mL of spent adsorbent sludge was centrifuged at 2000 rpm for 5 minutes.

TEST #6 Spherical Agglomeration

Spherical agglomeration was attempted following the method described by Rowat (1980). In a one liter Waring blender 100 mL of spent adsorbent and 100 mL of water were mixed for 4 minutes at high speed followed by 2 minutes of mixing at low speed. The resulting mixture was poured onto a 100 mesh screen where the agglomerated product remained on the screen.

TEST #7 Boiling

A 50 mL aliquot of spent adsorbent sludge was agitated while gently boiling for approximately half an hour. The sample was then observed while it cooled and settled.

TEST #8 Demulsifier

Three drops of Witconate 702 (Witco Chemical Corporation) demulsifier were added to 50 mL of spent adsorbent sludge in a graduated cylinder. The cylinder was sealed with parafilm and manually shaken for about 20 seconds. The sludge was observed with time and the volume of the observed phases recorded.

2.4 Advanced Adsorption/Regeneration Tests

2.4.1 Minto Coal

2.4.1.1 Advanced Adsorption Tests

The most successful regeneration method for Minto coal was found to be screening and washing on a 200 mesh screen. However, this method would require the pre-screening of the Minto coal prior to adsorption. Thus, a slurry contactor/clarifier adsorption test was conducted using Minto coal that was pre-screen on a 200 mesh screen and the fraction less than 200 mesh discarded. The test was conducted at one dosage (60 g/L) using the same methods described in Section 2.2.

2.4.1.2 Advanced Regeneration Tests

The screening process for regeneration of spent Minto coal was quantified by the following method. A carefully weighed sample of spent adsorbent sludge was screened on a 200 mesh screen and the screen washed with a known volume of HPLC grade water. The weight of the portion of the sludge and water that went through the screen was determined. The solids, water, and oil content of the sludge and

the obtained sludge fractions were determined by the Dean and Sark Analysis method (Rowat 1980).

2.4.1.3 Leaching Studies

In order to evaluate the potential for successive reuse of Minto coal, a leaching test and a jar test using leached Minto coal were conducted. The purpose of the leaching test was to serially leach Minto coal to determine if the pH continues to be depressed upon addition of Minto coal after serial leaches and to determine the amounts of some specific inorganic contaminants leached over a series of leachings.

The Minto coal used for this test was pre-screen and the fraction less than 200 mesh was discarded. The coal was serially leached using 1L of Burlington tap water to 60 g of coal. The coal was contacted for one hour by mixing with a magnetic stirrer and the slurry filtered on Watman #1 filter paper. The pH of the filtrate was determined and the leaching repeated until the pH did not change. The leaching water and the filtrate from the first and last leachings were analyzed for Ca, Mg, Fe and total silica.

A slurry contactor/clarifier adsorption test was conducted using dryed leached coal. The test was conducted at one dosage (60 g/L) using the same methods described in Section 2.2.

As a result of the leaching test results, it was hypothesized that iron played a significant role in the destabilization of the emulsion. To test this hypothesis, a jar test was performed in which Fe^{3+} was used in place of the adsorbent. The Fe^{3+} was in the form of ferric chloride and was dosed at a level

equivalent to the iron that would be leached from 60 g/L of Minto coal.

2.4.1.4 Destabilization/Filtration Test

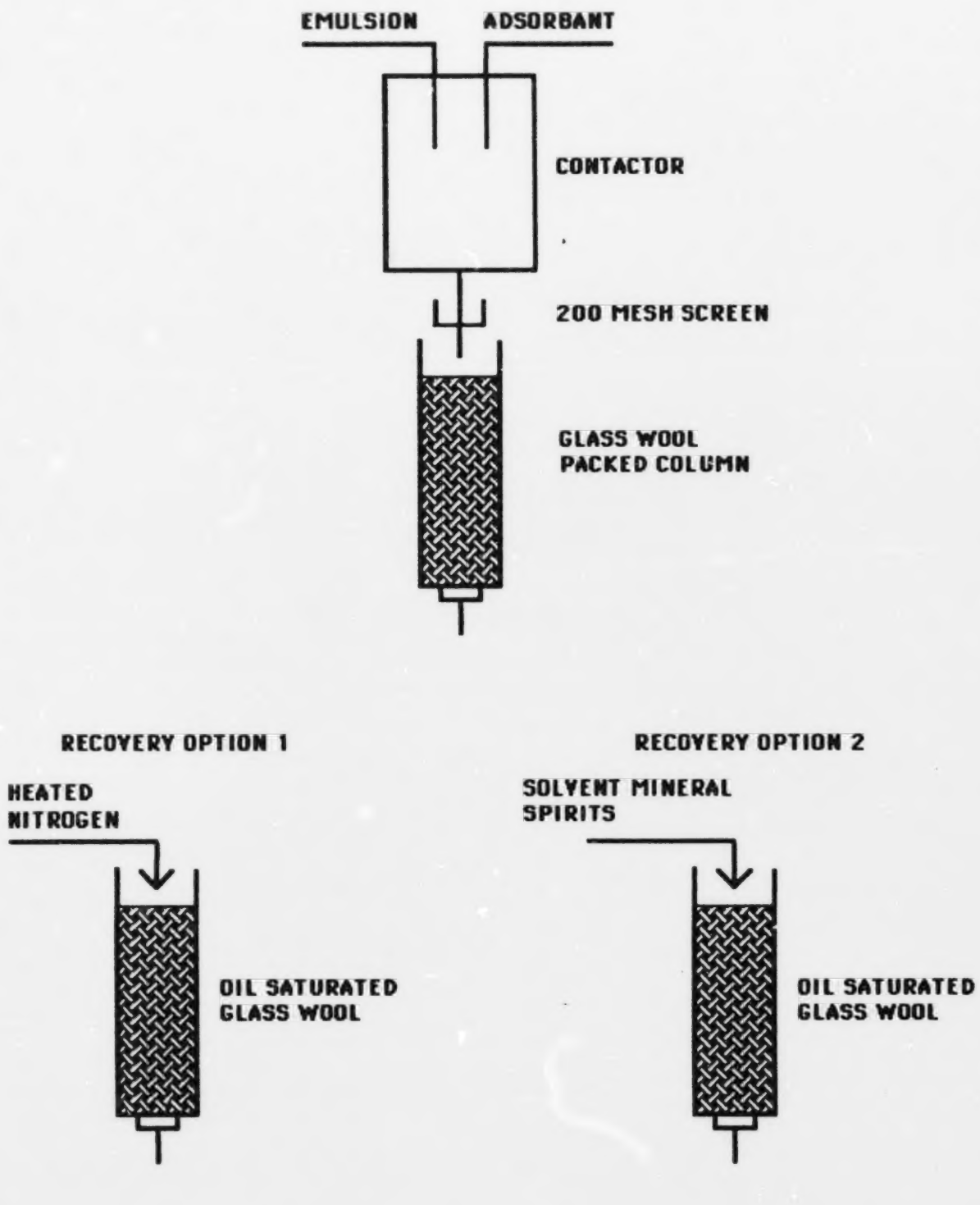
An alternative method of oil recovery based on Minto coal treatment was evaluated. In this experiment one liter samples of produced water were destablized by contact with 60 g/L Minto coal for 10 minutes in the slurry contactor and then fed through a 200 mesh screen to remove the Minto coal. 100 mL of the destabilized produced water was then fed through a column (ID 2.2 cm) packed to a depth of 8 cm with a weighed sample of glass wool. The effluent was analyzed for pH and TSO. A schematic of the oil recovery test is shown in Figure 2-1.

Two methods of recovery of the oil deposited on the glass wool were evaluated. In the first case the oil saturated glass wool was heated to 104°C. Nitrogen which was heated to 104°C was then fed to the top of the column at a pressure of 2 psi. After one hour the temperature of the column and the gas was increased to 150°C. After the second hour the gas pressure was increased to 8 psi. The recovery test was run for four hours. The amount of recovered oil was monitored with time.

The other oil recovery method investigated utilized a solvent to dissolve the oil in the column. The solvent used was a volatile mineral spirit which is a mixture of C9 to C12 hydrocarbons with a boiling point range 151°C - 216°C. 100 mL of solvent was fed through the column at approximately 1 mL/min. To accomplish this flow, pressure was required for the first 30 mL throughput to overcome

Figure 2 - 1

OIL RECOVERY TEST SCHEMATIC



the resistance to flow caused by the loading of oil on the column. This pressure was applied with a manually operated piston. The effectiveness of the extraction with respect to solvent volume throughput was judged by the colour of the effluent and the total amount of oil recovered was determined.

2.4.2 Fly Ash

2.4.2.1 Advanced Adsorption Tests

In order to establish adequate mixing times for fly ash contact, the fly ash slurry contactor/clarifier adsorption test described in Section 2.2 was repeated with a fixed dosage (60 g/L) and variable mixing times (10 min, 1 hour, 6 hours, 24 hours).

2.4.2.2 Advanced Regeneration Tests

Regeneration Test #7 (boiling) was repeated on a larger, weighed sample of spent fly ash sludge and the resulting phases weighed. The solids, water, and oil content of the sludge and the obtained sludge fractions were determined by the Dean and Sark Analysis method (Rowat 1980).

2.5 Coagulation Destabilization/Precipitation Tests

The advanced adsorption tests indicated that coagulation by metallic cations was a potential method of treatment for produced water. Thus a preliminary study was undertaken to assess the potential of a number of multivalent cations for coagulation of produced water. The coagulants evaluated were calcium chloride, alum,

ferric chloride and vanadium chloride. The coagulation tests were performed using the jar test techniques as described by numerous authors (Holden, 1970). The tests were conducted according to the flow chart shown in Figure 2-2. The raw and treated wastewaters were analyzed for pH and TSO. The equipment used in the coagulation tests was the same equipment used in the contactor/clarifier tests.

An initial jar test was run using six dosages (0-10 mM/L) of ferric chloride. The pH was adjusted with NaOH or HCl such that the pH after coagulation would be in the low solubility range for iron and aluminum (pH 5-6). The results of this test were used to establish suitable dosages to use in the jar tests with alum, calcium chloride and vanadium chloride. For these coagulants two dosages each were examined at a pH in the 5 to 6 range.

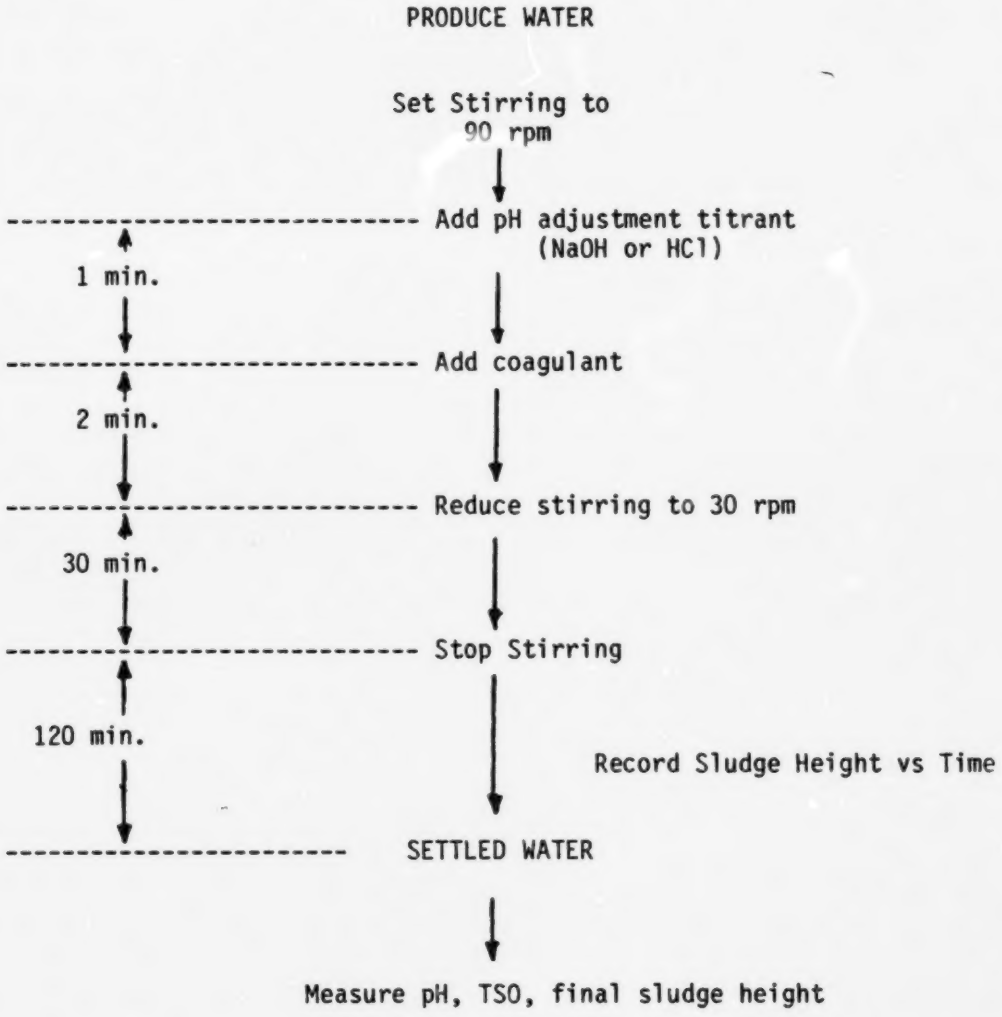
2.6 Alternate Adsorbent Tests

The advanced adsorption tests indicated that the presence of multivalent cations was critical in the removal of oil by Minto Coal. Thus alternate solid adsorbents which would provide a multivalent cation source were evaluated for the treatment of produce water. The methods used were the same as those used for the slurry contactor/clarifier adsorption tests.

The solids used in these tests were pyrite, iron oxide and vanadium oxide. Pyrite and iron oxide were dosed at 40 g/L and 80 g/L. Vanadium oxide was tested at one dosage (40 g/L) because of it's high cost. The pH in each jar was pre-adjusted such that the pH after solid addition was approximately 5.0.

FIGURE 2-2

COAGULATION TEST FLOW CHART



3.0 RESULTS AND DISCUSSION

3.1 Emulsion Characteristics

Upon receipt, the wellhead emulsion samples were visually examined and observed to be quite variable. The amount of floating free oil ranged from 0 to approximately 50 mL/L while the amount of settled material ranged from 0 to 300 mL/L. Most, but not all of the samples foamed when shaken. These results were consistent with the observed characteristics of the samples received in Phase I.

The results of the characterization of the composited, skimmed and decanted emulsion from Phase I and Phase II are shown in Table 3-1. The physical/chemical characteristics of the Phase II emulsion were quite consistent with the Phase I emulsion. The visual appearance, Ca and Mg were almost the same for both composite emulsions. The TSO of the Phase II emulsion was 23% lower than the Phase I emulsion and the iron concentration was about eight times greater than for the Phase I emulsion.

3.2 Contactor/Clarifier Adsorption Behavior

Table 3-2 shows the results of the initial slurry contactor/clarifier adsorption test for Minto coal. Relatively clear, clean supernatents were obtained in this test. The observed settling was zone settling (discrete sludge/supernatent interface). The initial settling velocity ranged from 0.4 m/h at a dosage of 30 g/L to 0.2 m/h at 80 g/L. These settling velocities are adequate for clarifier operation.

As predicted, the TSO values are dependent on adsorbent dosage. Figure 3-1 shows the isotherm obtained for the removal of TSO

TABLE 3-1

EMULSION CHARACTERISTICS

Parameter	Phase I	Phase II
pH	7.65	7.67
TSO (mg/L)	30,700	22,900
Fe (mg/L)	0.6	5.0
Ca (mg/L)	5.4	<6
Mg (mg/L)	1.16	1.6
Alkalinity (mg/L $CaCO_3$)		128

TABLE 3-2

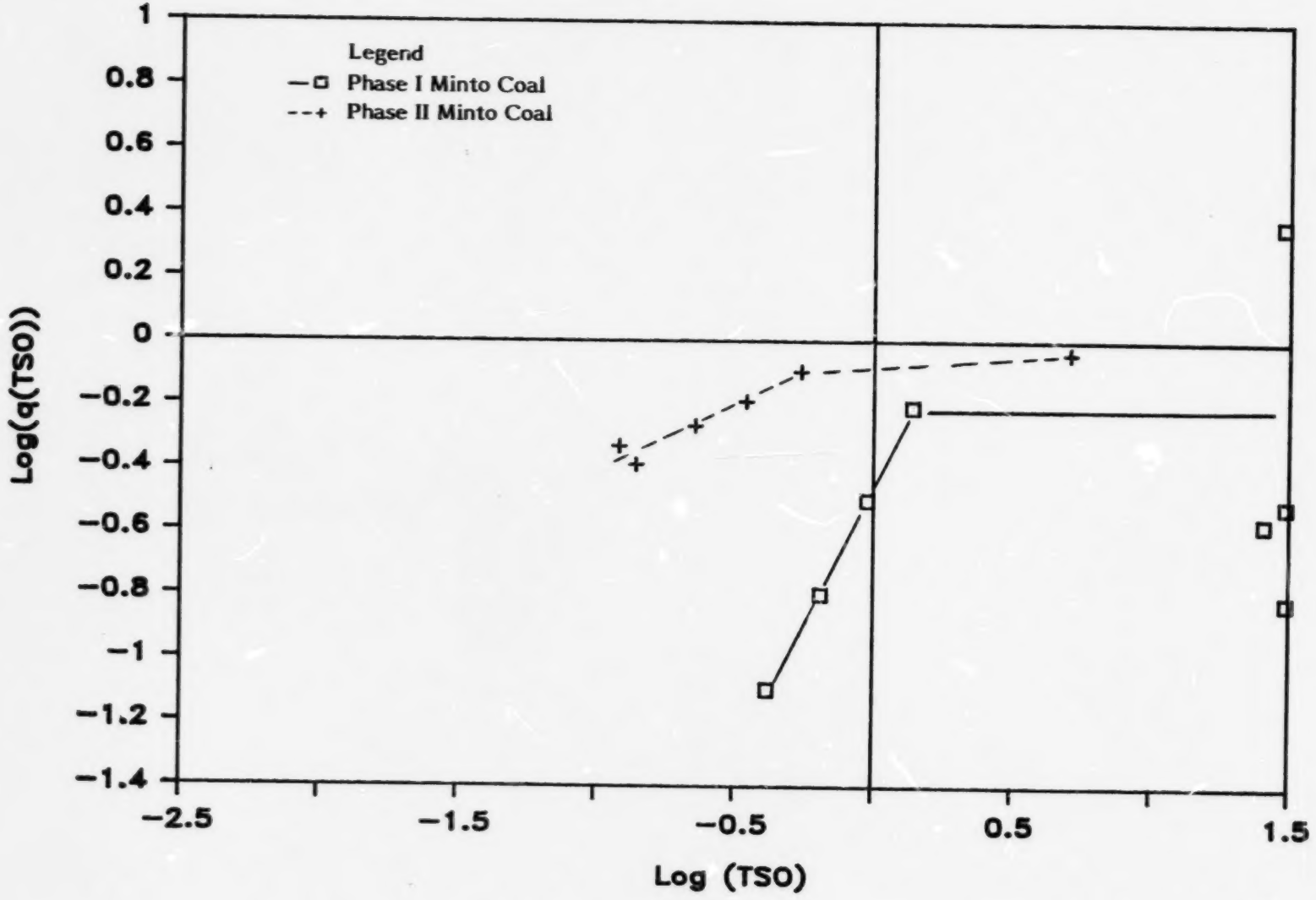
MINTO COAL SLURRY CONTACTOR/CLARIFIER ADSORPTION TEST

1L jars, no pH adjustment, mix 10 min. at 100 rpm

Dosage (g/L)	30	40	50	60	70	80
pH	5.96	5.82	5.66	5.49	5.23	4.94
TSO (g/L)	5.11	0.548	0.348	0.228	0.182	0.140
Type of Settling	Zone	Zone	Zone	Zone	Zone	Zone
Initial Velocity (m/h)	0.4	0.4	0.3	0.2	0.2	0.2
Initial Sludge Height(cm)	13	13.5	13	14	13	13
Final Sludge Height (cm)	1	1.8	3.0	2.8	2.8	3.6

Figure 3 - 1

ISOTHERMS FOR THE ADSORPTION OF TSO BY MINTO COAL



and the Minto coal isotherm developed in Phase I. The Phase II isotherm is more favourable but also contains the double slope observed for the Phase I isotherm.

Settling and clarification was not observed for fly ash contact/clarification with 10 minutes mixing at 100 rpm. Therefore, the jar test was repeated with 24 hours of mixing at 100 rpm and clarification was observed within the first 15 minutes of quiescence. The fly ash appeared to settle quickly (within the first 5 minutes) while clarification appeared to take much longer (more than 15 minutes). The observed clarification was flocculant type settling. The jars were allowed to settle 24 hours before pH and TSO analysis.

In Phase I the fly ash adsorption was shown to occur within the first five minutes of contact. However, in the Phase I kinetics experiements, the spent adsorbent was separated from the aqueous phase by filtration through glass wool and not by settling. Thus the contactor/clarification adsorption test indicates that although the removal kinetics may be rapid considerable energy input is necessary for the destabilized or adsorbed oil to settle.

The results of the fly ash jar test are shown in Table 3-3 while Figure 3-2 shows the isotherm obtained for the removal of TSO and the fly ash isotherm developed in Phase I. The Phase II isotherm is very similar to that obtained in Phase I.

3.3 Preliminary Adsorbent Regeneration Tests

The experimental results of the preliminary adsorbent regeneration tests are summarized in Table 3-4. At the outset of this phase it was envisioned that the spent adsorbents could be regenerated

TABLE 3-3

FLY ASH SLURRY CONTACTOR/CLARIFIER ADSORPTION TESTS

1L jars, no pH adjustment, mix 24 hours at 100 rpm

Dosage (g/L)	30	40	50	60	70	80
pH	10.69	11.15	11.18	11.31	11.37	11.22
TSO (g/L)	1.41	0.99	0.261	0.215	0.231	0.174
Type of Settling	F*	F*	F*	F*	F*	F*
Initial Velocity (m/h)	-	-	-	-	-	-
Initial Sludge Height (cm)	13	13	13.5	13	14	13
Final Sludge Height (cm)	3.2	3.5	3.5	3.5	3.5	3.5

*F - flocculant

Figure 3 - 2

ISOTHERMS FOR THE ADSORPTION OF TSO BY FLY ASH

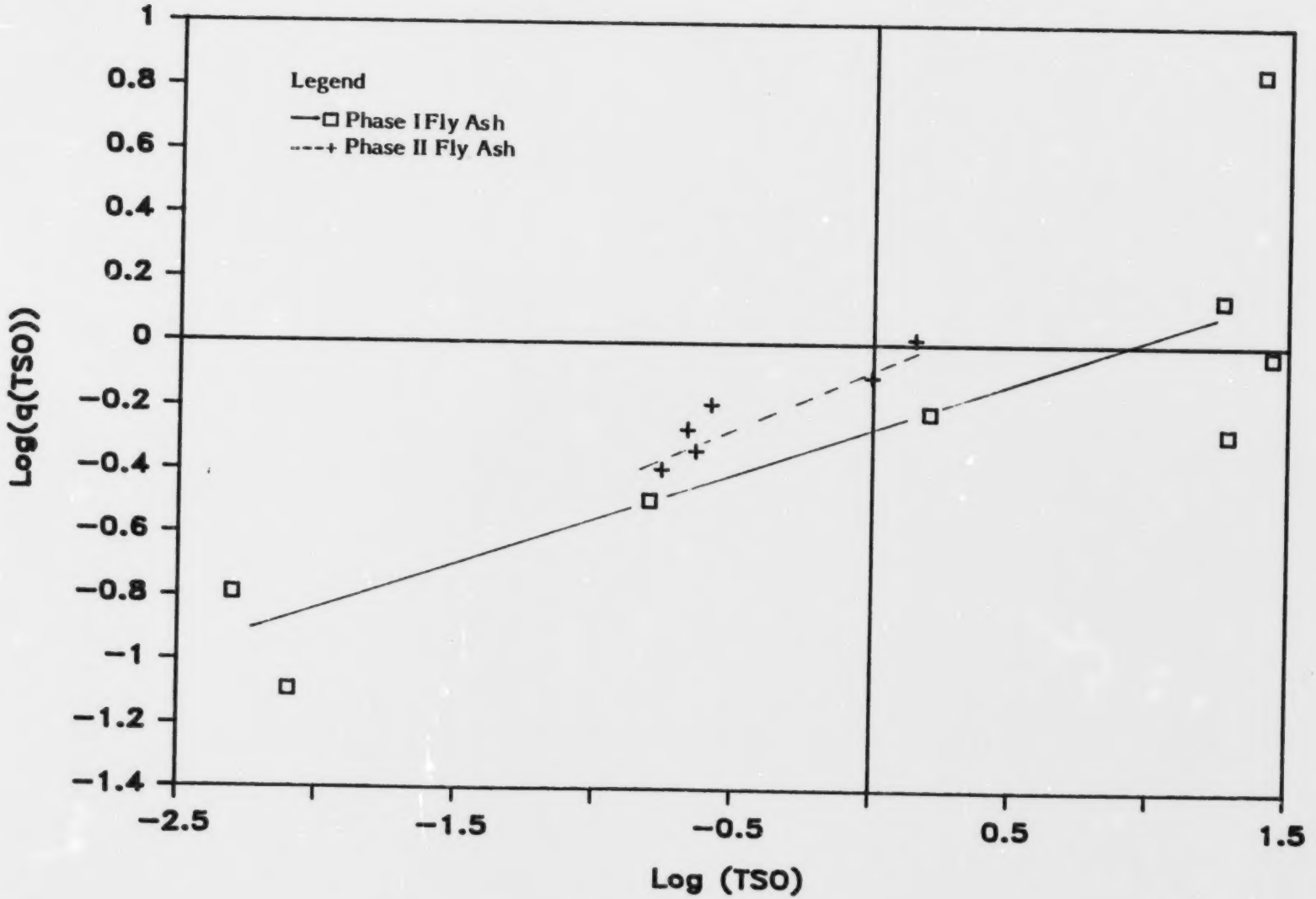


TABLE 3-4

PRELIMINARY ADSORBENT REGENERATION TESTS

Test	Minto Coal	Fly Ash
#1 DIRECT HEATING	-oil did not flow off coal. -upon cooling the mass had become solid and brittle.	-oil did not flow off ash.
#2 BOILING WATER WASH	-water separated but sludge remained	-no oil/ash separation.
#3 CAUSTIC WATER WASH	-created a stable emulsion	-created a stable emulsion.
#4 SCREENING	-with minimal agitation oil phase went through screen. -no binding or clogging. -oil phase small amount of solids. -coal phase can be washed with small amount of water. -this appears promising.	-sludge binds on screen. -ash goes through.
#5 CENTRIFUGATION	-no separation of oil/coal. -cloudy aqueous layer gathered on top.	-no separation of oil/solids. -cloudy aqueous layer gathered on top.

TABLE 3-4 CONT'D

Test	Minto Coal	Fly Ash
#6 SPHERICAL AGGLOMERATION	-formed a stable emulsion.	-irregular spheres (0.5-1cm) of oil and ash formed. -large amount of oil and ash remained non-agglomerated.
#7 BOILING	-no significant change upon cooling, some of the oil "coagulated" but contained coal.	-sludge foamed and expanded to three times original volume. -upon cooling three phases developed: 1.free oil which could be separated; 2.clear aqueous phase; 3. thick sludge ash/oil/water. -this appears promising.
#8 DEMULSIFIER	-no change	-water was driven out of sludge. -oil/ash sludge remained.

by direct application of heat to the dewatered adsorbents or by washing with hot water or hot caustic. Table 3-4 shows that none of these three methods (Test #1, #2, #3) resulted in recovery of adsorbed oil or regeneration of spent adsorbents for either Minto coal or fly ash. Thus a number of other potential regeneration methods were examined for the spent adsorbents.

For the regeneration of spent Minto coal the most promising method examined was screening (Test #4). Using this method, coal larger than 200 mesh could be retained on the screen and washed with a small amount of clean water. The fraction of the spent adsorbent sludge that goes through the screen is still an emulsion but the oil has been concentrated by a factor between 4 and 5. In this initial test, it was observed that coal fines also went through the screen into the concentrated oil sludge fraction. A solution to this problem would be to pre-screen the coal before use to eliminate the coal fraction smaller than 200 mesh. A sample of unused Minto coal was screened and 25% by weight of the coal was smaller than 200 mesh.

All other regeneration methods tried for spent Minto coal did not result in recovery of oil or regeneration of the adsorbent.

The regeneration of spent fly ash was found to be more difficult than for Minto coal. The most promising method was boiling (Test #7). Using this method free oil was released from the oil/water/solid sludge and floated to the surface. Futhermore, a clear clean aqueous phase developed under the free oil and a relatively clean looking fly ash layer developed at the bottom. However, in the middle, below the clean aqueous phase, a layer of oil/water/solids developed. This "middlings" layer did not disappear with longer

boiling times. Further development would be necessary to establish if the "middlings" problem could be overcome.

As shown in Table 3-4, all other regeneration methods tried for spent fly ash did not result in recovery of oil or regeneration of the adsorbent. However, two of the methods examined were successful in dewatering the sludge to obtain aqueous phase and an oil/solid phase. This however does not facilitate recovery of oil but it may be useful if it is necessary to burn the oil/solid product to recover the adsorbent.

3.4 Advanced Adsorption/Regeneration Tests

3.4.1 Minto Coal

3.4.1.1 Adsorption of Pre-Screened Minto Coal

The slurry contactor/clarifier adsorption test using pre-screened Minto coal (Minto >200) showed that screening Minto coal prior to use does not significantly effect the adsorption of TSO or the clarification process. Table 3-5 shows the results of the jar test using pre-screened Minto coal. Using pre-screened Minto coal results in a slightly higher residual TSO value and a slightly slower initial settling velocity. Furthermore the spent adsorbent sludge is slightly less dense. This slight deterioration of performance is not serious if it enables the use of a simple regeneration method.

3.4.1.2 Regeneration of Pre-Screened Minto Coal

The sludge obtained from the Minto >200 jar test was regenerated using the screening method. Table 3-6 shows the amount of sludge that was retained by the screen and the amount that passed

TABLE 3-5

ADVANCED ADSORPTION TEST: PRE-SCREENED MINTO COAL

Adsorbent	Minto Coal	Minto >200
pH Adjustment	None	None
Adsorbent Dosage	60 g/L	60 g/L
pH	4.46	4.41
TSO	97 mg/L	117 mg/L
Type of Settling	zone	zone
Initial Velocity	0.16 m/h	0.10 m/h
Initial Sludge Height	12 cm	12.8 cm
Final Sludge Height	3 cm	4.6 cm
Calculated Concentration of Solids in Sludge	240 g/L	167 g/L
Calculated Concentration of Oil in Sludge	92 g/L	64 g/L

TABLE 3-6

SUMMARY OF RESULTS: COAL SLUDGE SCREENING REGENERATION

Screened 75 mL of Minto >200 sludge on a 200 mesh screen and washed with 75 mL of clean water.

75 mL of sludge	72.72 g
75 mL of water	75.0 g
Total Weight	147.7 g
Weight through screen	134.1 g
Weight retained on screen	13.6 g

through. Table 3-7 shows the results of the Dean and Sark analysis of the Minto >200 sludge, the coal retained on the screen and the oil/water emulsion passed through the screen. This shows that the spent adsorbent sludge contains over 10% oil and close to 30% solids. Screening this sludge reduces the solids content to approximately 1.6%. The oil is partially diluted by the wash water. Table 3-8 is a mass balance of the solids and oil in the process. This shows that 98% of the solids are retained on the screen and that 91.2% of the oil is recovered in the emulsion that passed through the screen.

A 50 mL aliquot of the emulsion that passed through the screen was allowed to settle overnight and the emulsion dewatered such that 21 mL of clear water was obtained. The resulting sludge would be expected to contain 10.8% oil. The sludge was treated with the demulsifier Witconate 702 and the emulsion appeared to break immediately. The oil was allowed to settle overnight. 25 mL of clear colourless aqueous phase and 4 mL (4.03 g) of "free oil" were obtained. The amount of oil is consistent with the Dean and Sark analysis. Chemical demulsification is usually expensive when large amounts of emulsion must be treated. However, for the treatment of high oil concentrates such as the screened sludge the use of demulsifiers may be an economic option.

3.4.1.3 Minto Coal Leaching Study

The results of the analysis of the leaching medium and the serial leachates are summarized in Table 3-9. The leaching medium used was Burlington tap water. The analysis of the leachates shows that the pH depressing action of the coal is lost by the third

TABLE 3-7

DEAN AND SARK ANALYSIS OF COAL

SLUDGE AND SCREENED COAL SLUDGE FRACTIONS

A) Minto Coal Sludge

Solids	0.2716 g/g
Water	0.5898 g/g
Oil	0.1062 g/g

B) Screened Sludge Coal (13.6 g from 72.7 g)

Solids	0.6318 g/g
Water	0.3444 g/g
Oil	0.0558 g/g

C) Screened Sludge Oil/Water (134.1 g from 72.7 & 75.0)

Solids	0.001574 g/g
Water	0.9525 g/g
Oil	0.0629 g/g

Tabe 3 - 8

MASS BALANCE SOLIDS AND OIL MINTO COAL SLUDGE

Solids

On Screen (g/g of sludge)		Through Screen (g/g of sludge)	Total (g/g of sludge)
$0.6318\ (\frac{13.6}{72.7})$	+	$0.001574\ (\frac{134.1}{72.7})$	
0.1182	+	0.00290	0.1211
98%	+	2%	100%

Oil

On Screen (g/g of sludge)		Through Screen (g/g of sludge)	Total (g/g of sludge)
$0.0558\ (\frac{13.6}{72.7})$	+	$0.0629\ (\frac{134.1}{72.7})$	
0.01043	+	0.1150	0.1264
8.2%	+	91.8%	100%

TABLE 3-9

MINTO COAL SERIAL LEACHING STUDY RESULTS

Leaching Medium

pH 7.50 Total Silica 1.28 mg/L

Fe 0.1 mg/L Ca 68 mg/L Mg 10.9 mg/L

Alkalinity 46.4 mg/L $CaCO_3$

Leachate #1

pH 3.51 Total Silica 2.22 mg/L

Fe 350 mg/L Ca 114 mg/L Mg 16.3 mg/L

Leachate #2

pH 6.29

Leachate #3

pH 7.46

Leachate #4 - Final

pH 7.49 Total Silica 2.42 mg/L

Fe 0.6 mg/L Ca 68 mg/L Mg 12.4 mg/L

leaching. During the first leaching, 350 mg of iron, 0.94 mg of silica, 46 mg of Ca and 5.4 mg of Mg were leached from 60 g of Minto coal after 4 leachings the amount of these inorganics that were being leached were 0.5 mg of iron, 1.14 mg of silica, less than 1 mg of Ca and 1.5 mg of Mg. Obviously the parameter most susceptible to leaching is the iron. This metal is released in extremely large quantities in the first leach and is rapidly depleted by serial leaches.

A well known property of soluble iron is its destabilizing effect on suspended clays and colloids. Thus the possibility that iron may play a significant role in the destabilization of the emulsion was investigated.

Table 3-10 shows the results of jar tests using ferric chloride as an Fe^{3+} source and using Minto coal that had been leached four times with tap water. The results showed that ferric chloride alone destabilized and precipitated the emulsified oil whereas pre-leached Minto coal was totally ineffective for removing suspended oil. This indicates that the iron which is released from the Minto coal is the important factor in the oil precipitation.

Comparison of ferric chloride and virgin Minto coal jar tests results in Table 3-10 shows that ferric chloride is slightly more effective at reducing the TSO level but that the initial settling velocity and the sludge oil concentration is lower than for the virgin Minto coal. This indicates that the Minto coal acts as a coalescing surface or as a weighting medium which aids in settling of the destabilized oil.

TABLE 3-10

ADVANCED ADSORPTION TESTS: IRON CHLORIDE AND PRE - LEACHED MINTO COAL

Adsorbent	Minto Coal	Leached Minto	$FeCl_3$
pH Adjustment	None	None	13.75 meq OH^-
Adsorbent Dosage	60 g/L	60 g/L	6.25m M (349 mg Fe/L)
pH	4.46	7.62	5.44
TSO (mg/L)	97	21,600	28
Type of Settling	zone	none	zone
Initial Velocity (m/h)	0.16	--	0.05
Initial Sludge Height (cm)	12	--	11.0
Final Sludge Height (cm)	3	--	3.8
Calculated Concentration of Solids in Sludge (g/L)	240	--	1.9*
Calculated Concentration of Oil in Sludge (g/L)	92	--	60.2

* Calculated if all Fe precipitated as $Fe(OH)_3$

3.4.1.4 Destabilization/Filtration Test

An alternative treatment method based on Minto coal treatment was evaluated following the procedures described in Section 2.4.1.4. The emulsion treated in this test contained 28,050 mg/L TSO.

One liter of well-head emulsion destablized by contact with 60 g Minto was passed through a 200 mesh screen to recover the coal. 62 g (103%) of dryed coal was recovered. This indicates that probably all of the coal and possibly a small portion (approx. 8%) of the oil was recovered.

A 100 mL aliquot of the destablized emulsion was then fed through a column containing 6.29 g (0.20 g/cm^3) of Pyrex wool. Using only gravity feed this procedure took approximately 2 hour. During the first five minutes the flow was about 3 mL/min however this decreased to less than 0.5 mL/min by the end of the run. The oil penetrated the glass wool bed to a depth of 5 cm after 30 mL had been fed through the column, however, the oil "wave front" did not penetrate past this point as more emulsion was fed through the column.

The pH of the influent and the effluent were both 4.7. This pH is consistent with the slurry contactor/clarifier tests (see Table 3-5).

The effluent TSO was 0.24 mg/L. This is well below the limits for once through-steam generators (<1 mg/L) or cooling water make-up (<1 mg/L) discussed in the Phase I report.

A "blank" test was run in which 100 mL of untreated produce water was fed through a glass wool column. The influent to the column contained 27,600 mg/L TSO and the effluent contained 27,500 mg/L TSO. This confirms that the oil removal on the column is dependent on

initial emulsion destabilization by contact with Minto coal.

A possible mechanism for this oil removal process is as follows. Upon addition of Minto coal the emulsion is destabilized by the iron that is released by the coal and the oil begins to agglomerate or coalesce. When the destabilized emulsion is fed through the glass wool column the oil droplets either coalesce on the glass fibers, are filtered by the glass fibers or a combination of both phenomena.

Two operations for the recovery of the oil on the glass wool were attempted as described in section 2.4.1.4. The attempt at oil recovery by heating with heated nitrogen was not successful. The oil saturated glass wool column was calculated to contain 2800 mg of oil. When the nitrogen was initially introduced to the column 8.0 mL of oil/water emulsion were pushed from the column. This emulsion contained 475 mg of oil. A further 238 mg of oil was subsequently recovered over the entire heating cycle. In total 25% of the oil was recovered and of that 67% was obtained in the form of a concentrated oil/water emulsion. The potential of this recovery method appears to be limited as the tendency of the oil to flow even under high temperatures and pressures appears to be too low.

Solvent extraction with volatile mineral spirits was a more successful method for the recovery of the adsorbed oil. The glass wool column used for this test was calculated to contain 2800 mg of oil. Extraction with 100 mL of solvent recovered 2200 mg of oil which is a yeild of 79%. The solvent used was completely immiscible with water. The first 9 mL of effluent was clean clear water which had been pushed through the column by the solvent. The first 30 mL of

solvent effluent was highly coloured (dark brown) and contained 1400 mg of oil. The second 30 mL of effluent contained 600 mg of oil and the last 40 mL contained 200 mg of oil. Towards the end of the extraction, the effluent was straw coloured.

After the extraction the glass wool was observed to be covered with a dark solid. This solid is likely $Fe(OH)_3$ and continued reuse of this column without removal of this solid would not be possible. It is possible that this solid may be removed by backwashing or dissolution with acid.

3.4.2 Fly Ash

3.4.2.1 Advanced Adsorption Tests

In order to establish adequate mixing times for fly ash slurry contactor/clarifier adsorption tests were performed with variable mixing times. For mixing times of 10 minutes and 1 hour clarification was not observed within 3 hours of quiescence. After 6 hours and 24 hours clarification was observed within 15 minutes of quiescence. However, 6 hours of mixing at 100 rpm ($G \approx 150s^{-1}$) the energy and space required would be economically prohibitive. It is possible that the use of polymers or other settling aids would make the use of fly ash as an adsorbent feasible.

3.4.2.2 Advanced Regeneration Studies

Regeneration Test #7 (boiling) was repeated on a larger, weighed spent fly ash sample. The weights and compositions of the spent fly ash sludge and the resulting phases are shown in Table 3-11. As shown in the table, a water phase with low oil and solids content

TABLE 3-11

SUMMARY OF RESULTS: FLY ASH SLUDGE BOILING REGENERATION

Boiled 88.6 g of fly ash sludge and obtained three phases.

Fly Ash Sludge	
Composition	0.14 g/g oil
	0.32 g/g solids
	0.54 g/g water
Phase #1 "Free Oil"	4.72 g
Composition	0.29 g/g oil
	0.19 g/g solids
	0.52 g/g water
Phase #2 "Water"	6.21 g
Composition	0.006 g/g oil
	0.007 g/g solids
	0.98 g/g water
Phase #3 "Fly Ash"	77.6 g
Composition	0.14 g/g oil
	0.35 g/g solids
	0.51 g/g water

was obtained. However, the solids/oil separation in the "free oil" phase and the "fly ash" phase was not good. Although boiling results in some oil/solids separation significant technological development is required before it could be a viable regeneration method.

3.5 Coagulant Destabilization/Precipitation Test

3.5.1 Effect of Coagulant Dosage

The effect of coagulant dosage on TSO removal and settling velocity was evaluated for ferric chloride coagulation. The results of this test are shown in Table 3-12. The observed settling velocities were not significantly affected by the coagulant dosage. The initial settling velocities were between 0.12 m/h and 0.14 m/h. In general, settling velocities should be greater than 0.2 m/h for effective clarifier operation. Coagulant aids such as polymers or other flocculants can often be used to excellerate settling velocities such that traditional clarifiers can be used effectively. The TSO removal was significantly effected by the coagulant dosage. Figure 3-3 shows that as the coagulant dosage is increased the residual TSO is decreased. This is not a linear effect and the benefits attained by using ferric chloride dosages greater than approximately 5 mM/L may not be economically justified. A more detailed study would be required to determine the economic optimum dosage.

3.5.2 Effect of Inorganic Cation Type

One bivalent and three trivalent coagulants were evaluated on their ability to destabilize the produced water emulsion and

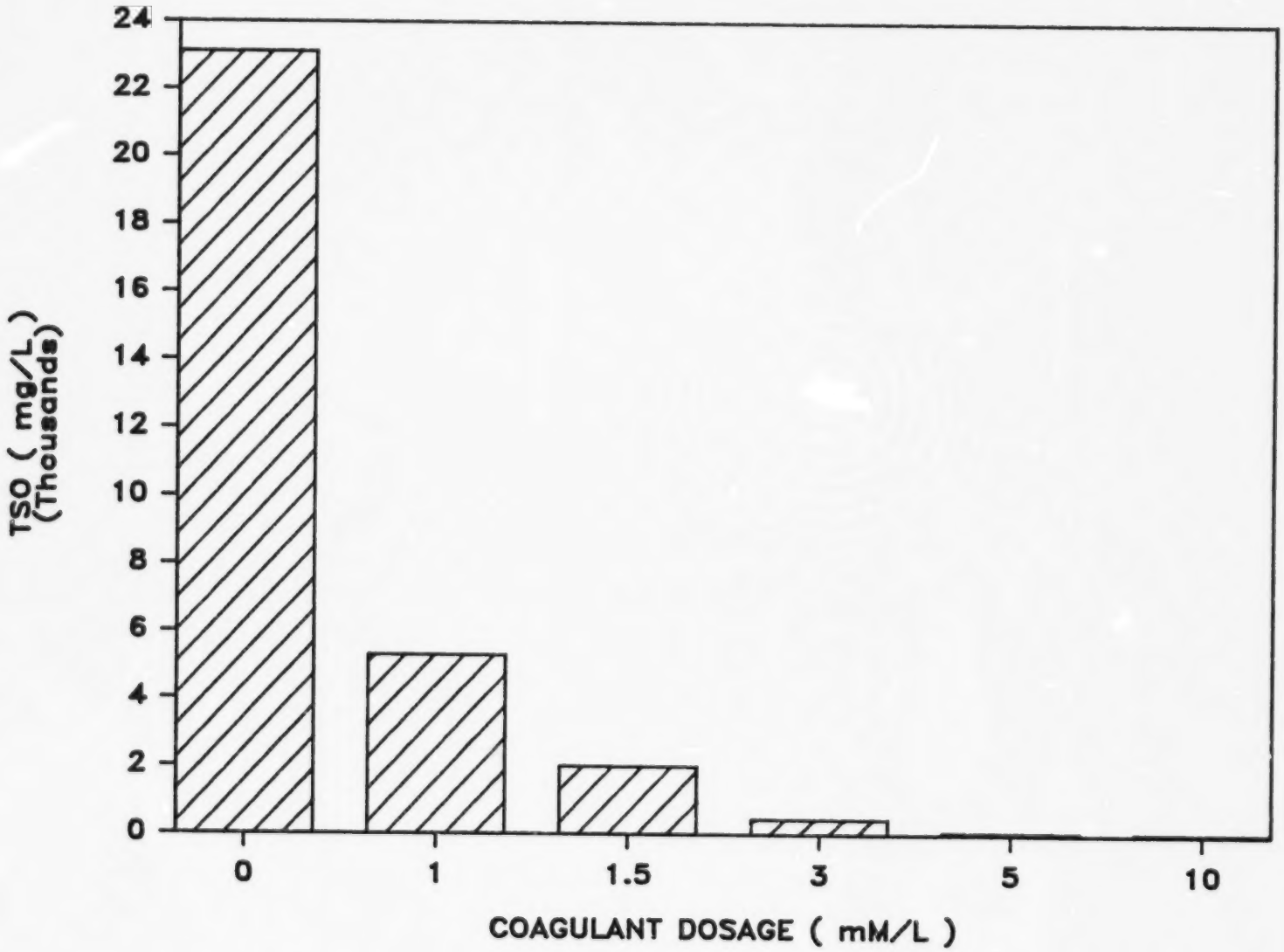
TABLE 3-12

FERRIC CHLORIDE COAGULATION TEST: EFFECT OF COAGULANT DOSAGE

Dosage $FeCl_3$ (mM/L)	0	0	1	1.5	3.0	5.0	10.0
pH control	0	4.4mL 1N HCl	1.4mL 1N HCl	0	4.6mL 1N NaOH	10.6mL 1N NaOH	25.6mL 1N NaOH
Final pH	7.1	5.1	5.7	5.6	5.6	6.0	5.9
Initial Sludge Height (cm)			11.7	12.2	11.9	12.0	12.7
Final Sludge Height (cm)				1.7	3.0	4.2	5.0
Settling Velocity (m/h)				0.13	0.14	0.12	0.12
TSO (mg/L)	23125	21500	5275	2000	440	69	34

Figure 3 - 3

EFFECT OF COAGULANT DOSAGE ON TSO RESIDUAL LEVELS
FOR FERRIC CHLORIDE COAGULATION



precipitate the oil. Table 3-13 shows the results of the jar tests for these coagulants.

The bivalent cation coagulant, calcium chloride, was observed to be totally ineffective for destabilization of the produced water emulsion. The jar test for calcium chloride was repeated at pH of approximately 9. This test was also unsuccessful for destablizing the emulsion.

The trivalent cation coagulants alum, ferric chloride and vanadium chloride, were very effective for the destabilization of the produce water emulsion and precipitation of the oil. The residual TSO levels were similar for these three coagulants at the higher dosage examined (5.0 mM/L). However at the lower dosages examined alum and vanadium chloride were more effective than ferric chloride.

Coagulant dosage did not significantly effect settling velocity except in the case of alum. With alum increasing the dosage from 2.5 to 5.0 mM/L more than doubled the settling velocity. The fastest settling velocity attained was 0.18m/h and was attained with alum at the high dosage. As discussed earlier for effective clarifier operation settling velocities should be greater than 0.20 m/h thus none of the observed settling velocities were sufficient for clarifier operation. The vanadium chloride settling velocities were significantly lower than the alum and ferric chloride settling velocities.

The concentration of oil in the sludge can be estimated from the final sludge height. These values are also included in Table 3-13. The highest sludge oil concentrations were obtained with ferric chloride followed by alum then vanadium chloride.

TABLE 3-13

COAGULATION TEST: EFFECT OF INORGANIC CATION TYPE

Coagulant	Calcium Chloride		Alum		Ferric Chloride		Vanadium Chloride	
Dosage (mM/L)	2.5	5.0	2.5	5.0	3.0	5.0	2.5	5.0
pH control	3.8 mL 1N HCl	3.8 mL 1N HCl	3.1 mL 1N NaOH	10.6 mL 1N NaOH	4.6 mL 1N NaOH	10.6 mL 1N NaOH	1.4 mL 1N NaOH	8 mL 1N NaOH
Final pH	5.3	5.2	5.6	5.9	5.6	6.0	4.9	4.6
Initial Sludge Height (cm)	12.5	12.5	12.2	11.5	11.9	12.0	12.5	12.2
Final Sludge Height (cm)			6.2	4.7	3.0	4.2	6.0	5.5
Settling Velocity (m/h)			0.081	0.18	0.14	0.12	0.057	0.06
TSO (mg/L)	21399	23162	84	112	440	69	92.5	82.5
Calculated Concentration of Oil in Sludge (mg/L)			46000	57000	92000	67000	49000	52000

3.6 Alternative Adsorbents

Three alternative adsorbents, pyrite, ferric oxide and vanadium oxide were evaluated in jar tests. The results of these tests are included in Table 3-14. The only successful solid adsorbent was ferric oxide (Fe_2O_3). Ferric oxide reduced the TSO to 9,450mg/L with a dosage of 40 g/L and to 34mg/L with a dosage of 80 g/L. Pyrite and vanadium oxide reduced the TSO approximately 30% and 20% respectively. If a readily available source of ferric oxide was available ferric oxide could be used as an "adsorbent" in a manner similar to that proposed in the Phase I report. However a method of oil recovery and oxide regeneration would be required. This process is likely to be very expensive to do the large quantity of sludge (approx. 50% of the initial feed volume) that would have to be processed.

TABLE 3-14

ALTERNATIVE ADSORBENTS

Adsorbent		Pyrite		Ferric Oxide		Vanadium Oxide
Dosage (g/L)	0	40	80	40	80	40
pH control	4.4mL 1N HCl	3.6mL 1N HCl	1.8mL 1N HCl	1.1mL 1N HCl	0.25mL 1N HCl	1.6mL 1N HCl
Final pH	5.1	4.5	5.9	5.4	5.0	5.6
Initial Sludge Height (cm)		12.0	12.5	12.5	12.0	12.5
Final Sludge Height (cm)					6.0	
Settling Velocity (m/h)					0.10	
TSO (mg/L)	21,500	15,920	14,400	9,450	34	17,250

4.0 TECHNICAL EVALUATION

4.1 Minto Coal

This study has shown that virgin Minto coal (fines removed) can effectively destabilize wellhead emulsions from in-situ bitumen/heavy oil recovery operations. The most likely mechanism for this destabilization is coagulation by iron released from the Minto coal upon contact with water.

Two possible processes, precipitation and filtration, utilizing the destabilizing effect of Minto coal were evaluated in this study. The destabilized emulsion can be precipitated in a traditional clarifier. Addition of polymers or flocculating agents may be required to increase the settling velocity to maintain adequate clarification. The TSO in the effluent of such a clarifier would be expected to be about 200 mg/L. This level of TSO would require further "polishing" to reach boiler feed water requirements. The concentrated oil sludge which is generated in this method can be fed through a screen to remove the coal particles and the oil can be released from the concentrated oil filtrate using a de-emulsifying chemical.

An alternative method of clarification of the destabilized emulsion that was shown to be effective was filtration. With this method, the coal could be immediately removed from the destabilized emulsion immediately after the contact period using a screen. The oil from the destabilized emulsion can be successfully filtered with a glass wool filter. The TSO in the effluent from this filter would be approximately 0.24 mg/L. This oil level would not required any further polishing steps before using as boiler feed. The oil

deposited in the filter has been shown to be 79% recoverable by solvent extraction. Optimization of this process would likely lead to much greater recoveries.

The major drawback to using Minto coal is that it is not regenerable. Although the Minto coal can be easily recovered its emulsion destabilizing effect is decreased by leaching and has been shown to be completely ineffective after being pre-leached 4 times with tap water.

4.2 Fly Ash

Fly ash has been shown to destabilize the wellhead emulsion however excessive energy input is required to promote effective settling of the oil. It may be possible that flocculant aids could be used to overcome this problem. Another problem is that the settled oil cannot be easily separated from the fly ash. The most promising regeneration method appears to be boiling in water. However, viability of this technique is dependednt on successful development of the method to promote more complete oil/solid separation.

Tests completed in Phase I of this project showed that fly ash will destabilize wellhead emulsions sufficiently to allow removal of the oil by filtration through glass wool. However, fly ash cannot be easily removed from the emulsion prior to glass wool filtration and serious problems due to the deposition of fly ash in the filter would have to be overcome before this is a technologically viable process.

Overall fly ash has not been shown to be a technologically promising alternative for the treatment of wellhead emulsions.

4.3 Coagulants

Trivalent metallic coagulants have been shown in this study to be very effective for destabilization and precipitation of wellhead emulsion. Jar tests indicated that the clarifier overflow after treatment with a trivalent metallic coagulant would likely contain in the order of 100 mg/L of TSO. This TSO level would require further polishing to meet boiler feedwater requirements. The observed settling velocities were not quite fast enough for traditional clarifier operation but this problem should be readily overcome by process optimization.

Coagulation/precipitation is widely used in potable water treatment and has been used successfully in the treatment of a diverse range of wastewaters. It is a well developed technology that is relatively well understood mechanistically. Coagulation has the advantage of removing dissolved organic as well as suspended material in one step. Development of this process for the treatment of wellhead emulsion appears to have significant technological merit.

Alum and ferric chloride are relatively inexpensive, readily available coagulants. Vanadium chloride is expensive, not widely available and did not appear to have any technological advantage over alum or ferric chloride and thus should not be considered for process devleopment. Further process development is required before an accurate technological and economic assessment of a coagulant precipitation and oil recovery process can be made. The process should be optimized with respect to coagulant dosage and pH and the use of flocculant aids to improve settling velocity should be

considered. The effect of elevated temperatures on floc formation and settlability should also be assessed. Other metallic coagulants such as the polymeric aluminum coagulants could also be evaluated. Sludge handling and oil recovery will required special investigation. The process of separating water, metal hydroxice and oil must be developed for this to be a viable oil recovery process.

Another coagulation process which may have technological advantages over traditional coagulation/precipitation is emulsion destabilization by metallic coagulant addition and immediate filtration on a media such as glass wool. The Minto coal study results suggest that this process may reduce the TSO level to less than 1 mg/L. Using a coagulant rather than Minto coal would be advantageous because expensive coal slurrying and coal screening steps could be eliminated. The filtration process may be superior to the precipitation process as smaller coagulant dosages may be sufficient to destabilize the emulsion for filtration than are required for flocculation and precipitation. Furthermore the oil can be obtained in a more concentrated form in a column than in a sludge thus possibly simplifying oil recovery operations.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following is a summary of the conclusions of the final phase of this study.

i) Oil removal by Minto coal is a result of emulsion destabilization caused by the leaching of iron.

ii) Good emulsion destabilization and settling can be obtained with virgin Minto coal.

iii) Minto coal can be recovered from the concentrated oil sludge by screening on a 200 mesh sieve and the oil can be released for the concentrated oil filtrate using a de-emulsifying chemical.

iv) Emulsion destabilization is not obtained using Minto coal that has been pre-leached 4 times with tap water.

v) Glass wool filtration of wellhead emulsion that has been destabilized by contact with Minto coal results in an effluent with less than 1 mg/L TSO. Furthermore oil can be successfully recovered from the glass wool column be extraction with a volatile mineral spirits solvent.

vi) Excessive energy input is required to promote effective settling of oil when treated with fly ash.

vii) Oil coated fly ash cannot be regenerated easily. The most promising regeneration method appears to be boiling in water. However, viability of this technique is dependent on successful development of the method to promote oil/solid separation.

viii) Trivalent metallic coagulants (alum, ferric chloride, vanadium chloride) are very effective for destabilization and precipitation of wellhead emulsion.

ix) Coagulation/precipitation treatment of wellhead emulsion with trivalent metalic coagulants results in residual TSO levels in the order of 100 mg/L.

x) Calcium chloride, a bivalent metallic coagulant does not effect emulsion stability.

xi) Slurry contact/clarification with ferric oxide results in emulsion destabilization and precipitation however, extramely large sludge volumes would preclude this treatment from being a viable wellhead emulsion treatment option.

xii) Slurry contact with pyrite or vanadium oxide does not result in emulsion destabilization.

5.2 Recommendations

This study has shown that multivalent cations are effective for the destabilization of wellhead emulsions. The following specific recommendations are made for future studies.

i) Optimum conditions for coagulation/clarification by precipitation with aluminum or iron coagulants should be established by bench scale testing. To optimize this process, the effects of coagulant type, coagulant dosage, pH, temperature, and flocculant aids should be evaluated.

ii) The use of de-emulsifying chemicals or solvents for the recovery of oil from the coagulation sludge should be investigated.

iii) The process of removal of oil by filtration of emulsion destabilized by coagulation should be developed and optimized in bench scale studies. The optimum coagulant type, coagulant dosage and filter media should be determined. Filter media other than glass wool that should be considered are synthetic fibers, sand, anthracite, and Minto coal.

iv) A method of oil recovery and column regeneration for the above process should be developed. Methods which should be considered are solvent extraction, steam extraction, and backwashing.

v) The applicability of the above processes should be demonstrated on wellhead emulsions from a number of in-situ bitumen/heavy oil recovery sites.

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APPENDIX A

ANALYTICAL PROTOCOL

ANALYTICAL PROTOCOLS

Total Suspended Oil (TSO) and Total Suspended Solids (TSS)

1) Filter known volume (v) of sample through a washed, ashed and preweighed (w_1) Whatman glass fiber filter.
2) Dry filter overnight at 100°C.
3) Weigh filter (w_2).
4) Ash filter. Care must be taken to increase temperature slowly from 150°C to 450°C to volatilize oil without burning. Muffle for 1 hour at 450°C.
5) Weigh filter (w_3).
6) Calculations:

$$TSO = \frac{W_2 - W_3}{V} \qquad TSS = \frac{W_3 - W_1}{V}$$

note: Weigh loss at 100°C assumed to be only water - along with water loss there may be a loss of the low-boiling components of the oil - resulting in a low TSO value.

Filtered Organic Carbon

1) Filter sample through a prewashed Whatman GFC glass fiber filter.
2) Determine TOC using a Beckman Model 915 TOC analyzer (Beckman Instruments, Inc. Fullertan, California) following method described in operating manual.

Silica

Silica is determined on a filtered aliquot following the procedure described in AWWA Standard Methods 15/B (Molybdosilicate Method).

Calcium, Magnesium and Iron

1) Filter sample through a prewashed Whatman GFC glass fiber filter.

2) Determine metals concentration using a Jarrel-Ash Atomic Absorption Spectrometer Model 82-500 (Jarrel-Ash Inc. Waltham, Mass.) following methods described in operating manual (Calcium Analytical Method No. 9, Iron Analytical Method No. 15, Magnesium Analytical Method No. 18).

3) **Total Hardness** is calculated by multiplying the concentration of each cation by the proper factor to obtain equivalent calcium carbonate, and by summing these $CaCO_3$ concentrations. If present in significant amounts, other hardness-producing cations must be determined and included in the computation. To obtain the $CaCO_3$ equivalent (mg/L) of the following cations, multiply the concentrations found (mg/L) by the factor shown below. (Environment Canada Analytical Methods Manual 1979)

Cation	Factor
Ca	2.497
Mg	4.116
Sr	1.142
Fe	1.792
Al	3.710
Zn	1.531
Mn	1.822